

PROBE FOR DETERMINATION OF OXYGEN ACTIVITY IN METAL MELTSAND METHODS FOR ITS PRODUCTION.

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Field of the Invention

This invention relates to a probe for the measurement of the oxygen activity of metal melts, in particular steel melts and to a method for producing this probe

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Background of the Invention

US 4 906 349 discloses a known generic probe. This probe is part of a measuring head that is to be immersed into the melt and in this example comprises a small tubelet protruding out of the measuring head and made out of stabilized zirconium oxide which is at high melt 15 temperatures (about 1500°C up to 1800°C) predominantly oxygen conducting and negligibly electron conducting. The small tubelet is closed at the protruding end and located therein is a reference substance in form of a powdery mixture of chrome and chrome oxide which is connected with a measuring instrument by an electric conductor. The measuring instrument is furthermore connected to an electron conducting bathcontact and therefore measures the 20 potential difference between the melt and the reference substance, so that having regard to the temperature the oxygen activity in the melt can be calculated.

The principle of the measurement of the oxygen activity with such probes is also disclosed in the article "Sauerstoffmeßsonde FOX für Stahlschmelzen" in the journal "Stahl 25 und Eisen" 95 (1975), No. 22, page 1084.

From the US patents 3 752 753 and 3 773 641 embodiments are known where not the small tubelet as a whole is made out of a solid electrolyte but just a plug is cemented into the open end of a small refractory tubelet, whose plane outer front side is in contact with the melt during the measurement.

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Finally, embodiments are known where a solid electrolyte is used as a coating on a carrier pin or on a small carrier tubelet, as can be seen in DE 28 33 397 A1. These probes have an extra small reaction time.

10 Probes of the described type have become standard as measuring elements for the oxygen activity especially for controlling the development of the deoxidation process with aluminum. Their function is in the range of high oxygen levels, that is from 100ppm to 1000ppm or more, quite satisfactory.

15 However, it was remarked that the reliability, accuracy and especially the reproducibility of the measurement is unsatisfactory in the range of low oxygen levels from 1ppm to 100 ppm.

20 This problem is also dealt with in the already mentioned US 4 906 349. There the probes are mechanically cleaned on their outer surface to be immersed in the melt by etching or grit blasting in order to allow measuring at oxygen concentration from zero to 20ppm with a higher precision and with an improved reaction time.

25 The mechanical and chemical cleaning of the surface pointing into the melt of a solid electrolyte like zirconium oxide is not easy and requires an considerable additional expenditure.

One of the objects of the invention is improve functionality of the said probes at low oxygen concentrations without further expenditure and without further risk.

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### Summary of the Invention

This problem is solved by a further development of the known probe, wherein the entry surface of the solid electrolyte is coated by a functional foil arrangement. A foil arrangement in this sense can be a single foil or a couple of foils located one upon another 10 exerting a particular function when immersed into the melt.

The expression "foil" in the present context is to be taken as the opposite of a coating. The foil is a sheet-like element, e.g. a thin rolled metal sheet, that holds together without a 15 special carrier. It is a flat sheet-like element of small thickness, which is essentially constant over the surface area.

The function of the foil comprises various features. The perturbation of the measurement at low oxygen concentrations can partly be explained by the fact that upon 20 immersing of the probe into the melt on the surface of the probe oxygen is drawn in from the neighborhood and is then measured, too. This error is becoming considerable if the oxygen level of the melt is particularly low.

Another function of the foil could be the influence on the wettability of the entry 25 surface by the melt. If the foil is made of such material which does not hinder the migration of the oxygen ions from the melt to the solid electrolyte and at the same time under the influence

of the melt during melt open has an advantageous effect on the wettability, such errors of the measurement can be reduced.

The foil arrangement as a whole and especially its single foils should be flexible so 5 that they can easily fit the shape of the entry surface of the solid electrolyte and can fit to it in close contact. The foil arrangement correspondingly should possess only a small mechanical rigidity.

To provide the entry surface of the solid electrolyte of a probe of the kind discussed 10 with a covering is principally known.

In US 4 342 633 the small tubelet of the solid electrolyte is provided with a push-over screen of a low carbon steel which is to reduce the temperature shock when immersing of the probe into the melt. The screen surrounds the probe and has itself the shape of a small tubelet 15 fitted to the probe which can be shoved over the small probe tubelet with a tight fitting. The small steel tubelet, in contrast to the foil, has an inherent stability. This tight fitting is hard to achieve as the small tubelets of the solid electrolyte are producable only with some tolerances at the outer periphery. A close contact of the inner periphery of the small steel pipe to the outer periphery cannot be obtained. Air and oxygen will always remain in the interstice 20 between the steel tubelet and the electric tubelet and affect the measurement at low oxygen levels in the melt. The arrangement given in US 4 342 633 has therefore a purpose different from the invention and cannot fulfill the purpose of the invention.

The Japanese publications JP 56100353 A2, JP 56100354 A2 and JP 56092450 A2 25 disclose coatings of the solid electrolyte probe improving the measurement behavior of the probe in molten steel. In JP 56100353 A2 a coating is presented with a metal like Fe, Cu, Ni,

Mg, Al or similiar or a metal oxide like MgO, Al<sub>2</sub>O<sub>3</sub> or similiar made by vaporizing, sputtering, ion plating or another method. From JP 56100354 A2 the covering of the solid electrolyte with a metal oxide powder like MgO, Al<sub>2</sub>O<sub>3</sub> or similiar in an organic binder is known that results into an accelerated heat transfer and an improved process reaction rate. In 5 the third document an oxygen activity of about 35ppm, thus in the low level range, is mentioned. In JP 56092450 A2 a coating of a mixture of a metal powder and an organic binder to improve the wetability of the solid electrolyte probe through the molten steel is described. Between the probe and the steel no thermal isolating layer is to be established. This will reduce the starting time.

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The coverings in the form of coatings need an additional costly apparatus and bear the risk of chip-off upon immersing into the melt.

On the other hand, the coating of the entry surface with a foil arrangement according 15 to the invention has the advantage of a greater simplicity, and a chip-off like in a coating will not appear.

The foil arrangement can comprise at least one foil oxidable by oxygen in the melt and can for example consist of an aluminum material.

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Such a foil melts instantly upon the contact with the hot melt and reacts with the oxygen that may have been drawn in at the surface of the probe during immersion into the melt. This oxygen therefore cannot falsify the measurement any longer.

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The foil arrangement can comprise at least one further functional foil at least partly covering or overlapping the first foil.

It is preferred that the material of the further foil when melting supports the wettability of the entry surface of the solid electrolyte in contact with the melt so that it will have uniform contact with the melt.

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A foil with such a function can consist of a copper material. Further examples for the material of the further foil are Pb, Ag, Zn, Sn, Au, Pt, Bi, Mg.

In case the solid electrolyte is provided in form of a material having a substantially flat  
10 end wall in the end of a refractory small tubelet the foil arrangement can extend in front of this end wall.

However, if the solid electrolyte is provided in form of a small tubelet to be immersed into the melt and closed at the end to be immersed, the foil arrangement can surround the  
15 outer periphery of the small tubelet tightly.

A further development of the invention involves means of keeping the foil arrangement in close contact to the entry surface and reinforcing the contact.

20 Such means can comprise a binder located between the entry surface and the foil arrangement and disintegrating when in contact with the melt. Such a binder is to disintegrate and disappear by burning, vaporizing or dissolving in the melt after it provided the close contact to the entry surface until immersion.

25 Alternatively and preferably the means can be mechanical means which press the foil arrangement from outside into close contact with the entry surface.

The pressing can take place over the surface or elastically. A simple means of this kind which has already proven itself in practice comprises an elastomeric hose tightly surrounding the foil arrangement on the outer surface of the small tubelet.

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This hose may have at first a greater diameter than the foil arrangement surrounding the small tubelet and may be shrinkable in its radial diameter on to the foil arrangement after being shoven on it longitudinally.

10 This can be practically effected in that the hose is made of a material with a thermoactive shape memory.

The invention also has a process aspect according to which the small tubelet is surrounded tightly by a functional foil arrangement at its peripheral surface, where over the 15 foil arrangement located on the small tubelet a elastomeric hose is shoved over longitudinally whereafter the hose is shrunk onto the foil arrangement causing a radial pressure causing a close contact between the foil arrangement and the entry surface.

A hose made of a shape-memory material can be used and the hose is then heated 20 when in shoved-up position for shrinking.

The following non-limiting description along with accompanying figures is provided to more specifically teach and set forth particular embodiments of the present invention as envisioned here. They are for illustrative purposes only, however, and those skilled in the art should 25 understand that they can make various changes, substitutions and alterations herein without departing from the spirit and scope of the invention in its broadest form.

## **Detailed Description of the Invention**

Preferred Embodiments of the invention are illustrated in the accompanying  
5 figures.

Fig. 1 shows a longitudinal section of the lower part of a probe;

Fig. 2 shows a cross section along Line II-II in Fig. 1;

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Fig. 3 shows an analogue longitudinal section of a second embodiment;

Fig.4 shows a cross section along Line IV-IV in Fig. 3.

15           The probe which is referred to as a whole by numeral 100 in Fig. 1 comprises a small tubelet 1 comprising a cylindrical outer surface 1" and being approximately semispherical closed at the lower end. It is made of a solid electrolyte 11 which is at high temperatures predominantly oxygen ion conducting and negligibly electron conducting and which consists in this embodiment out of  $ZrO_2$  stabilized with  $MgO$ . The reference substance 2 consisting  
20           out of a mixture of Chrome and Chromeoxides is located in the lower part of the small tubelet 1. The inner surface 12 of the solid electrolyte 11 is at the outermost part of the lower end 1' in electrically conducting contact with a contact wire 3 leading to a measuring instrument. The outer surface of the lower end 1' is referred to as numeral 13. In practice, the small tubelet 1 has an outer diameter of about 5 mm and a total length of about 30 mm. Only  
25           the lower part is shown in Fig. 1. The small tubelet 11 together with a thermoelement and a bath contact, coupled to the measuring instrument as well, is located in a probe head (not

shown in the fig.) which is sunk into the melt from above at the top of a lance. The reference substance 2 has a known oxygen activity. The oxygen activity of the melt depends on its oxygen content. This results in a potential difference between the outer and inner surface of the small tubelet which can be measured via the measuring instruments and allows to 5 calculate the oxygen activity of the melt.

The small tubelet 1 at its outer peripheral surface area constitutes an entry surface 4 for the oxygen ions of the melt.

10 The entry surface 4 is wrapped tightly by a foil arrangement 10, being illustrated in the embodiment of Fig. 1 by a single foil 6 out of a aluminum material. In this embodiment the single foil 6 is wrapped once around the small tubelet 1. The edges slightly overlap at position 7 in Fig. 2, so that the whole surface of the small tubelet 1 is covered. At the lower end the foil 6 is folded around the surface 13 so that the complete outer surface of the small tubelet 1 15 is covered.

The foil 6 is itself surrounded by a hose 8 consisting out of a elastomeric material, which in the embodiment of Fig.1 is closed at its lower end 8' similarly to the small tubelet 1. The hose 8 has at first a cylindrical inner diameter slightly greater than the outer diameter of 20 the foil 6 wrapped around the small tubelet 1. In this state, the hose 8 can be pulled over the foil 6 to its total length and is then covering the foil 6 and the small tubelet 1 to their total extent including the lower end 1'. The hose 8 consists out of a shape-memory material and can be shrunk by heating so that a radial tension in the hose 8 is build up leading to a radial outside pressure on the foil 6, which brings the foil 6 into close contact to the entry surface 4 25 i.e. the outer surface of the small tubelet 1. In Fig. 1 and 2, the probe is refered to by 100 in its state ready for operation after the shrinking of the hose 8.

The presence of the foil 6 in close contact to the entry surface 4 of the small tubelet 1 leads to the consequence that upon immersion of the probe 100 into the melt no air oxygen can stick to the entry surface 4 build up by the outer surfaces 1",13 and thereby being drawn 5 into the melt and affecting the oxygen activity measurement. Immediately after the probe 100 is sunk into the melt, the hose 8 burns up. The resulting amount of carbon is so low that the measurement is affected in a negligible way only. After the disappearance of the hose 8, the foil 6 out of a aluminum material is oxidized by unwanted oxygen in the proximity of the entry surface 4. Therefore the foil 6 is in a sense catching away unwanted drawn-in oxygen.

10 Due to the very low mass of the foil 6, the measurement to follow is unaffected.

As far as in the probe 200 of Figs. 3 and 4 functional equivalent parts are present, these are referred to by the same numerals as with the probe 100 of Fig. 1 and 2.

15 The probe 200 differs from the probe 100 in that the foil arrangement 20 in this case is two-layered comprising beneath a radial outer foil 6 consisting out of an aluminum material a radial inner foil 9 out of a copper material, which when in contact with the melt after the disappearance of the hose 18 and the foil 6 improves the wettability of the entry surface 4 by the melt. The foils 6 and 9 are layered over each other on the whole surface. They may be 20 laminated or loosely positioned over each other. The foil arrangement 20 covers the cylindrical part 1" as well as the area 13 located at the lower end 1' of the small tubelet 1, too.

In contrast to the hose 8, in Fig. 3 the hose 18 is not closed at the lower end, but simply consists of a cut hose, which slightly extends over the lower part 1' of the small tubelet 1. After the pull-up of the hose 18 and the shrinking, the configuration as shown in 25 Fig. 3 is reached, in which the stickout part 18' has shrunk to a very much lesser diameter, merely leaving a small inner channel 18" which is outwardly open. This embodiment also

fulfills the function of a close contact of the foil arrangement 20 to the outer surface 1",13 of the small tubelet and is more economical than a closed hose 8.

It is clear that the foil arrangements 10, 20 may be wrapped around the small tubelet 1  
5 several times.

For better visibility, the thickness of the foils 6, 9 and the hoses 8,18 has been shown exaggerated. In practice, the foils have a thickness of about 0,02 to 0,05 mm. The shrinkable hose 8, 18 can have a wall thickness of about 0,2 to 0,5 mm.

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The shrinkable hose 8, 18 can in principle be omitted if the foil arrangement 10, 20 is equipped with a binder and glued around the small tubelet 1. The embodiment with a hose is preferred due to its better protection for the entry surface against oxygen drawn in during immersion into the melt.

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What is claimed:

1.) Probe (100) for the measurement of the oxygen activity of metal melts, in particular steel melts,

5 comprising a reference substance (2) in electrically conducting contact (3) with a measuring device;

and comprising a solid electrolyte predominantly oxygen ion conducting at high temperatures and negligibly electron conducting and separating the reference substance (2) from the melt and having an entry surface (4) for oxygen ions in contact with the  
10 melt,

wherein the entry surface (4) of the probe ready for operation is covered by a functional foil arrangement (10,20) in close contact to the entry surface(4).

2.) Probe according to claim 1, wherein the foil arrangement (10,20) comprises at least one  
15 foil (6) oxidizable by the oxygen contained in the melt.

3.) Probe according to claim 2, wherein the foil (6) consists out of a aluminum material

4.) Probe according to any of the claims 1 to 3, wherein the foil arrangement (20)  
20 comprises at least a further foil (9) at least partly covering the first foil.

5.) Probe according to claim 4, wherein the material of the further foil when melting due to  
the contact with the melt enhances the wettability of the entry surface (4) of the solid  
electrolyte (11).

6.) Probe according to claim 5, wherein the further foil (9) consists out of a copper material.

7.) Probe according to any of the claims 1 to 6, wherein the solid electrolyte is provided in form of a material having a substantially flat end wall at the end of a refractory small tubelet and the foil arrangement (10, 20) extends in front of said end wall.

8.) Probe according to any of the claims 1 to 7, wherein the solid electrolyte is provided in form of a small tubelet (1) to be immersed into the melt and closed at the end to be immersed with the reference substance (2) being located in the interior of the small tubelet and that the foil arrangement (10,20) totally and tightly surrounds the outer periphery of the small tubelet.

9.) Probe according to any of the claims 1 to 8, further comprising means to keep the foil arrangement (10,20) in close contact to the entry surface (4).

10.) Probe according to claim 9, wherein said means comprise a binder located between the entry surface (4) and the foil arrangement (10,20) and disintegrating when in contact with the melt .

11.) Probe according to claim 10, wherein said means are mechanical means, which press the foil arrangement (10,20) from outside into close contact with the entry surface (4).

12.) Probe according to claim 11, wherein said means press the foil arrangement (10,20) against the entry surface (4) over its extension.

13.) Probe according to claim 12, wherein said means push the foil arrangement (10,20) against the entry surface (4) in an elastic way.

14.) Probe according to claim 13, wherein said means comprise an elastomeric hose (8,18) 5 tightly surrounding the foil arrangement (10,20) on the outer periphery of the small tubelet (1) constituting the solid electrolyte.

10 15.) Probe according to claim 14, characterized in that the hose (8, 18) first has a greater diameter than the foil arrangement (10,20) surrounding the small tubelet (1) and that the hose is shrinkable in its radial diameter after being positioned longitudinally over the foil arrangement (10,20).

15 16.) Probe according to claim 15, wherein the hose (8,18) is made of a material with a thermoactive shape memory.

17.) Method of producing a probe (100,200) for the measurement of oxygen activity of metal melts, in particular steel melts, with the probe comprising an solid electrolyte predominantly oxygen conducting at high temperatures and negligibly electron conducting and intended to be immersed into the metal melt and having a entry surface 20 for oxygen ions, characterized in that the entry surface (4) is tightly covered by a functional foil arrangement (10,20); that over the foil arrangement (10,20) on the entry surface (4) a elastomeric hose (8,18) is positioned longitudinally and that then the hose (8,18) is shrunk onto the foil arrangement (10,20) causing a radial tension leading to a close contact between the foil arrangement (10,20) and the entry surface (4).

18.) Method according to claim 17; wherein the hose (8,18) is made out of a thermoactive shape memory material and the hose (8,18) is heated when in position.